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IMPROVED SPECIFICATIONS FOR COMPOSITE PROPELLANT BINDERS FOR AR--ETC(U)
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TECHNICAL REPORT RK-81-5

IMPROVED SPECIFICATIONS FOR COMPOSITE
PROPELLANT BINDERS FOR ARMY WEAPON SYSTEMS -
FINAL REPORT

James G. Carver
Propulsion Directorate
US Army Missile Laboratory



June 1981



U.S. ARMY MISSILE COMMAND

Redstone Arsenal, Alabama 35809

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A process has been developed that simultaneously can determine the molecular weight, molecular weight distribution, functionality, and functionality distribution of hydroxy-terminated polymers. The samples are analyzed on a high performance GPC permeation column and the detector responses sent directly to a computer. The molecular weight and molecular weight distribution are calculated using the universal calibration procedure. By reacting the polymer with a UV chromatograph, 3,5 dinitrobenzoyl chloride, the hydroxyl groups can be detected. By ratioing the UV response and the refractive index response, the hydroxyl groups per		

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molecule can be determined. Detailed procedures for calibration derivitization and analysis are provided. A computer program for data reduction written in Basic for a Hewlett-Packard Lab Automation System is also provided.

This project has been accomplished as part of the US Army Materials Testing Technology Program, which has for its objective the timely establishment of testing techniques, procedures, or prototype equipment (in mechanical, chemical or nondestructive testing) to insure efficient inspection methods for materiel/ material procured or maintained by DARCOM.

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I. INTRODUCTION

Current procedures for the analysis of polymeric binder materials for composite propellants are inadequate. They are time-consuming, ineffective, difficult to accomplish and, for these reasons, often neglected by the propellant manufacturer. Typical specifications call only for bulk properties of the binder, such as hydroxyl number and viscosity, and then look for impurities. These tests are insensitive to the many subtle, but significant, variations that can occur when a vendor modifies his procedure for preparation of the binder or even its starting materials. It is also possible, for example, for a vendor to adjust the viscosity of an unacceptable lot to meet the specifications by blending in high and/or low viscosity samples of the same polymer.

In a recent experience with one missile system, the vendor modified its synthetic procedure. The resulting binder met the specifications, but did not produce a good propellant. Following investigation it was found that the molecular weight had increased slightly. This caused materials with marginal solubility not to dissolve and a non-homogenous propellant resulted. If a specification for molecular weight had been present at the time, then the problem and resulting expenses could probably have been avoided.

Kermit Ramey has evaluated [1] several lots of hydroxyterminated polybutadiene (HTPB) which is the binder in several missile systems, including VIPER, PATRIOT, and MLRS. He compared two methods for determining molecular weight, Vapor Phase Osmometry (VPO), and Gel Permeation Chromatography (GPC). While the results were in good agreement in most cases, there were noteworthy examples where the VPO value was in error. Thus, the GPC was the preferred technique. Also in his report Ramey observed that the hydroxyl value was not constant through the molecular weight range of the polymer. As the molecular weight increased the hydroxyl value, or functionality, generally increased. Law and Levinthal [2] found a significant influence of the binder functionality distribution on the properties of resulting propellants. Thompson, McGee, and Walter [3] have also observed the effects on propellants' properties. In addition, Stephens, et al. [4] report that the properties for the propellant can be tailored by modifying the functionality of the high molecular weight fractions of the polymers.

It therefore appears desirable to characterize a binder prepolymer toward its molecular weight, molecular weight distribution, functionality, and functionality distribution. There currently exist several methods for molecular weight determination, but only one method, GPC, can give a good picture of the molecular weight distribution. One of the problems with GPC has been the development of an acceptable standard calibration procedure. Another problem is that the analysis is slow, requiring up to four hours per analysis. While the functionality can be determined by either of two equally acceptable methods, acetylation or reaction with toluene sulfonylisocyanate, the only procedure for determining the functionality distribution is to collect fractions of different molecular weights and determine the functionality of each fraction. This process can take up to two man-weeks per sample.

Therefore, a project was undertaken to develop a rapid GPC analytical procedure that can be easily calibrated. In addition, an effort was made to develop a procedure to determine the functionality distribution of a binder in less than four hours. This is the second and final report on the two-year

effort. The results of the first year's work have been published [5] and presented to the 1979 JANNAF Propellant Characterization Subcommittee Meeting.

II. DISCUSSION

A. Molecular Weight Distribution

One of the few propellant specifications that includes limits for molecular weight is the PATRIOT Missile System. The procedure described in that specification uses a GPC developed in the early 1970s and requires up to four hours per analysis. Understandably, multi-run analysis for statistical significance is seldom made. This can result in misleading or erroneous values. In every analysis there is the possibility of random error. In GPC the principle of random error cancelling out does not apply. The longer the run the greater the probability of error. When statistical analyses are made, typical variations are 5 percent to 12 percent [6,7,8,9]. In recent years significant advances have been made in high pressure chromatography. GPC columns have been made smaller and are able to withstand up to 2000 psi. This permits analytical runs to be made in less than 40 minutes, decreasing the probability of error.

In GPC several factors can introduce error [10]. The more significant factors include the choice of solvent, the sample concentration, the injection volume, choice of columns [11], flow [12], and temperature. These were all considered in the first year's effort and are discussed in that year's report [5]. The effect of temperature was inadvertently demonstrated during this work when the temperature control unit malfunctioned. Table 1 shows the effect of a small change in temperature of the column/solvent system. It was also observed that the materials in the GPC columns require up to two hours to equilibrate at operating pressures before reproducible data can be obtained (see Table 2). When all these variables can be optimized and controlled, the precision of the data improves to two to four percent, as shown in Table 3.

A method for analysis that can be used by several laboratories must not only be precise but accurate, as well. To achieve good accuracy the system must be well calibrated. The Q method, as described by Van Landuyt and Huskins [13], was attempted but the results were unsatisfactory [5]. The universal calibration method described by Grubistic [14] was selected as the method of choice. There are a great number of publications concerning this procedure [15,16,17,18,19, 20,21,22,23,24] and the accuracy is well demonstrated. The major problems associated with the method are that accurate intrinsic viscosities and molecular weights are required for the calibration, and that an intrinsic viscosity should be determined for each unknown polymer. It is

Table 1. Effect of Column Temperature

<u>Temperature</u>	<u>Mn</u>
25°C	2429
27°C	2530
30°C	2765

Table 2. Time for Equilibration

Sample Injected at	Retention Time
5 min	13.19 min
60 min	13.21 min
75 min	13.23 min
180 min	13.23 min
210 min	13.23 min

Table 3. HTPB-R45M Molecular Weights Precision and Accuracy (1978 data)

HTPB LOT	303285	303305	402195	708065	803105	803175	803205
VPO	2710	2790	2830				
HPLC	2772 $\pm 1\%$	2856 $\pm 4\%$	2874 $\pm 2\%$	2777 $\pm 1\%$	2235 $\pm 2\%$	2580 $\pm 2\%$	2370 $\pm 2\%$
Δ	+2.2%	+2.3%	+1.5%				

important that the temperature and solvent that the GPC are operating at are the same as used to determine the intrinsic viscosity. Table 1 has shown the effect of small differences in temperature and Table 4 demonstrates how an erroneous value in the calibration sample can influence the unknown apparent molecular weight. The calibration used in this project has been described previously [5].

A third method of calibration, and the most desirable, is the use of standard samples of the same polymer to be analyzed. Unfortunately very few types of polymer standards are available. For the hydroxyterminated polybutadiene (HTPB) materials a close relative is available. Both Goodyear Chemicals and Pressure Chemicals offer low molecular weight polybutadiene standards. Anderson [6] has examined these standards and determined that since there are nominally two relatively small hydroxyl groups per polymer molecule "These functional groups are unimportant in determining the hydrodynamic volume of the polymer." Therefore, a direct calibration of retention time versus molecular weight can be made using polybutadiene as standards for HTPB. Once the system has been calibrated for molecular weight, the calculation of \bar{M}_w and \bar{M}_n is rather straightforward using Equations (1) and (2), as outlined in ASTM D 3536-76.

$$\bar{M}_w = \frac{\sum A_i M_i}{\sum A_i} \quad (1)$$

Table 4. Influence of Calibration Intrinsic Viscosity

$[\eta]_{(117 \text{ Å})}$	\bar{M}_n (HTPB)
0.176	3324
0.19	3083
0.20	2929
0.21	2790

$$\bar{M}_n = \frac{\sum A_i}{\sum \left(\frac{A_i}{M_i} \right)} \quad (2)$$

Here A_i is the area under the curve of a fraction of the polymer with molecular weight M_i .

The system used in this project included a Waters Associates Model 201 liquid chromatograph (equipped with a Waters 401 refractive index detector), Waters Associates 100 Å, 500 Å, 10³ Å, and 10⁴ Å microstyragel columns, a Waters Associates Wisp 710B automatic liquid sampler, a Perkin-Elmer LC 55 UV detector, and a Hewlett-Packard 3353E laboratory automation system. (Two A/D converters are necessary for the computer to accept input from the detectors and an S/ECM to monitor the Wisp 710B.) The solvent, tetrahydrofuran, was from Burdick and Jackson Laboratories and was filtered prior to use. A nitrogen blanket was kept over the THF to prevent the formation of UV-absorbing peroxides.

Data were sent to the computer in area versus time slices. The slice width was chosen at four seconds, since this almost exactly matched the time lag between the detectors at a flow of 2.0 ml/min. The data were stored in the computer memory and analyzed by a basic program (see Appendix A) after the run was completed. Figure 1 represents a graph of the data presented to the computer. The program also includes a section that monitors the 710B and in the event of a problem can shut-off the LC system through power relays.

Basically the program polls the injector for its status and which bottle it injected. Then the program searches its file for the sample name and intrinsic viscosity. The stored data are then analyzed to determine the molecular weight of each slice i and the sums are made to calculate \bar{M}_n and \bar{M}_w . Each analysis, from injection of sample to printing of results, takes only 32 minutes. This is a great improvement over the previous methods that required four hours for the sample to elute and up to one-half day to calculate the results.

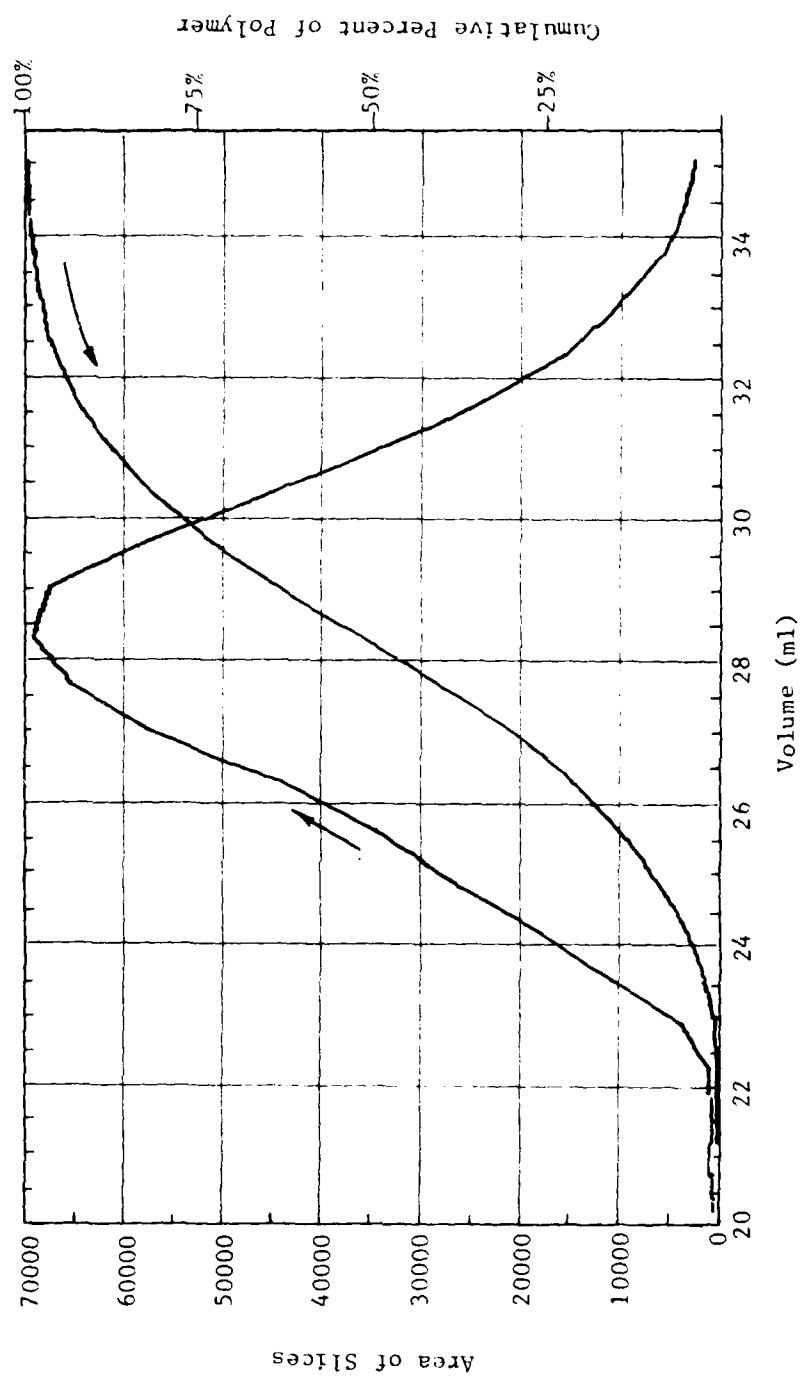


Figure 1. Computer representation of chromatographic run.

Since the system is easily automated from injection to data reduction, it is less difficult to get a large number of runs and statistically calculate the accuracy and precision of the process. Table 5 summarizes the results of several runs made in a one-month period. While the precision is not as good as in Table 3, it must be pointed out that Table 3 represents only two days' worth of data. Table 5 includes more runs and several samples of each lot. Since the lots used in this project were not stabilized with an anti-oxidant, and were between two and seven years old, some inhomogeneity between samples is expected. For these reasons the small loss in precision was not unexpected, but is still a significant improvement over the previous techniques. Table 6 demonstrates the day-to-day variation of samples of two lots is quite good.

B. Functionality Distribution

The second phase to this project was to develop a rapid method for determining the functionality and functionality distribution of a hydroxy-terminated polymer. The procedure selected involves derivatization of the polymer hydroxyl groups to make them absorb in the ultraviolet spectrum and then pass the polymer through a size exclusion column train. As the polymer elutes, it flows sequentially through a UV detector and an RI detector. The responses of the two detectors are ratioed, and calibrated response factors are applied resulting in a value representing hydroxyls/molecule. The basic concept of using two detectors to get chemical information had been described earlier [25]. A process [6,7] similar to that developed under this project was described in 1975, but the equipment limited their precision to seven percent and the derivatizing agent selected was highly reactive to water, causing handling difficulties.

In developing this procedure, the goals were that it be rapid, quantitative, simple, and not degrade the polymer. While the basic concept is similar to that of Baczek [6,7], it was developed independently. Derivatizing polymers to determine the functional group content by UV spectroscopy has been reported in several papers [26,27], but is limited to measuring the total functionality of the bulk polymer. There is extensive literature available on derivatizing alcohols [28-34], but is limited to measuring the total functionality of the bulk polymer. There is extensive literature available on derivatizing alcohols [28-34] for UV detection in liquid chromatography. The only problem therefore was to select the best derivative and calibrate the method.

Table 5. \bar{M}_n Analysis of HTPB-R45M (1980)

HTPB LOT	303285	402195	803105	803175	803205
VPO	2710	2830			
HPLC	2627 $\pm 3.8\%$	2722 $\pm 3.5\%$	2433 $\pm 3.6\%$	2320 $\pm 4.5\%$	2244 $\pm 5.1\%$
Δ	-3.1%	-3.8%			
No. Runs	41	41	30	43	35

Table 6. Day-to-day Variation of \bar{M}_n

303285				402195			
Day	Nr. of Points	\bar{M}_n	\pm	Day	Nr. of Points	\bar{M}_n	\pm
6	9	2536	3.3%	6	9	2674	2.7%
7	15	2621	3.3%	7	15	2672	3.2%
8	6	2671	2.7%	8	6	2707	2.6%
20	13	2713	4.1%	20	14	2831	4.8%
21	16	2983	4.2%	21	5	2862	2.6%
	ALL	2627	3.8%		ALL	2722	3.5%

Several derivatives were considered. Kovats [26] had developed a series of highly reactive siloxy groups with large extinction coefficients, but these were not commercially available. Phenylisocyanate has a good extinction coefficient, is readily available, and has been used in similar processes [6,7,27,30]. Evaluation of phenylisocyanate indicated that while it reacted quantitatively with the polymers' hydroxyl groups it had to be handled in a dry box and freshly distilled frequently. The λ_{\max} for the derivative was found to be at 243 nm. Jupille [28] discusses several other derivatives. The hydroxyl derivative used in liquid chromatography most often appears to be 3,5 dinitrobenzoate. It reacts slowly to atmospheric moisture and has a very large extinction coefficient at 254 nm, which almost any UV detector can monitor.

Several procedures for preparing the 3,5 dinitrobenzoate [29,32,33,34] have been published. Evaluation of these disclosed two problem areas common to all. First, the reaction employed pyridine as a catalyst. While this is an adequate catalyst in most processes, complete derivatization in this case required at least a one-hour heating of the sample. Heating an underivatized sample of the polymer to 60°C in either toluene or THF for one hour caused the sample to change color from pale yellow to dark brown. GPC analysis of these samples showed an increase in the number average molecular weight and a larger polydispersity. When the polymer was reacted with 3,5 dinitrobenzoyl chloride under these conditions, the functionality was observed to increase well above the known values. Second, the workups following the reaction leave significant quantities of both pyridine and 3,5 dinitrobenzoic acid in the sample. These interfere with the low molecular weight portion of the chromatogram. At the 10th JANNAF Propellant Characterization Meeting in June 1979, the use of *n*-methylimidizol (NMI) as a catalyst in acetylation reactions was discussed. A study of the catalytic effect on acetylation of hydroxyl compounds has also been published [35]. This has an imine nitrogen similar to pyridine, but does not absorb in the region of 254 nm. Investigation of NMI as a catalyst in the 3,5 dinitrobenzoate reaction was very successful. Heating the sample for only

15 minutes gives quantitative derivatization. The sample may even have been reacted in less time than this but it could not be verified. Comparison of the molecular weights of samples before and after being reacted usually showed an increase in molecular weight of less than 30. The functionalities calculated for the samples agreed well with known values, and the reaction solution appeared to be unchanged from time of mixing to 15 minutes at 60°C. Prolonged heating of the sample showed no change in the functionality until, after an hour, the sample showed signs of decomposition. The sample turned brown and the molecular weight and functionality started to increase significantly.

The problem with carrying the 3,5 dinitrobenzoic acid through the workup was removed with the procedure described by Carey and Perisinger [36]. That procedure, modified to use NMI, is as follows: In a small vial 4 ml of a dilute solution of the polymer in tetrahydrofuran (THF), about 0.1 g per ml (0.4 m moles of OH), 0.18 g of 3,5 dinitrobenzoyl chloride (0.8 m moles), and 2-3 drops of NMI are placed. The vial is then sealed, shaken, and heated to 60°C for 15 minutes. The solvent is then evaporated under a stream of nitrogen with gentle heating. Then the residue is dissolved in 2-3 ml of ether and washed with several portions of dilute sodium bicarbonate (two 1-ml washes with 5 percent NaHCO_3 are generally enough) and then water. The ether layer is then filtered and injected in the chromatograph directly. Sample holdup on the filter is apparently negligible or indiscriminant, since no change in the molecular weight was observed between filtered and unfiltered samples.

As stated earlier, the computation of the functionality is accomplished by ratioing the responses of the UV and RI detectors and applying a correction factor. To determine the response factor for the RI detector, several samples of different HTPB-R45M lots were prepared. Their concentrations ranged from 0.05 g per ml to 0.5 g per ml. Using a 1- μl and a 10- μl syringe, different volumes of each sample were injected using a Waters U6K injector. This model injector has a 200- μl sample loop, which is completely flushed by the solvent directly onto the column. Since all materials elute from a GPC column between V_e and V_t , it was assumed that the area under the curve represented all the polymer that was placed in the injector. The analog output of the detector was digitized by an A/D converter and the area under the curve computed by the Hewlett-Packard Lab Automation System.

Determining the response factor of the UV detector was accomplished by derivatizing a large nonfunctional aliphatic alcohol, undecyl alcohol. To avoid the possible loss of material, the sample was injected without being washed. Unfortunately, the 3,5 dinitrobenzoic acid interfered with the chromatogram. Therefore, the separation was accomplished with a reverse phase ODS column using 40 percent acetonitrile in water as the carrier. This gave a baseline separation of the derivatized alcohol. The response factor was determined in a manner similar to the RI. Least squares analysis of the data from both detectors indicated a linear response within the limits tested and a coefficient of determination (r^2) of 0.9999.

The procedure and calibration being complete, three samples each of six lots of HTPB-R45M from ARCO were reacted and analyzed. Table 7 indicates that, except for two lots, agreement of calculated F_n values with data supplied by ARCO is very good. The precision of the measurement of F_n is also excellent

Table 7. F_n Analysis of HTPB-R45M Precision and Accuracy

LOT	303285	402195	708065	803105	803197	803205
ARCO	2.23 ± 6'	2.20 ± 1	1.97	1.79	1.86	1.80
GPC	2.20 ± 4.6	2.20 ± 3.7	1.82 ± 6.0	1.84 ± 9.3	1.88 ± 2.7%	1.78 ± 4.0%
Nr. of Runs	29	27	10	16	8	9
Δ	-1.4	0	-7.6	-2.8	+1.1%	-1.1%

and frequently more than twice as good as previously reported [6,7]. Table 8 shows even better agreement of the calculated equivalent weights with the ARCO data. Figures 2 and 3 indicate the change in functionality and equivalent weight with molecular weight. It should be noted that the functionalities in Table 7 and equivalent weights in Table 8 are the average of three samples of each lot analyzed over a 15-day period. The sample-to-sample variation is very small. In fact, the samples of two lots shown in Table 9 are all within one standard deviation of each other.

To examine the effect of time on a derivatized polymer, several samples were analyzed over a 15-day period. It can be seen in Table 10 that for the first week after preparation the sample is fairly stable; but by the end of the second week some samples have become nonhomogeneous. This is probably due to attack by either light or oxygen, or both, on the polymer itself.

III. CONCLUSION

A procedure has been developed that can simultaneously determine the molecular weight and functionality of a hydroxy-terminated polymer. The time of preparation of a sample can be as short as one hour. Once the sample has been prepared an aliquot can be injected, analyzed, and the data reduced every 40 minutes. In this manner, a sample can easily be analyzed several times in one day and the data evaluated for statistical significance.

Table 8. Equivalent Weight Analysis of HTPB-R45M Precision and Accuracy

LOT	303285	402195	708065	803105	803175	803205
ARCO	1300	1300	1400	1250	1380	1320
GPC	1312 ± 5.3%	1365 ± 5.7%	1401 ± 4.8%	1287 ± 4.8%	1360 ± 1.8%	1318 ± 4.6%
Nr. of Runs	25	17	29	29	18	21
Δ	+0.9%	+5.0%	+0.1%	+3.0%	-1.5%	-0.2%

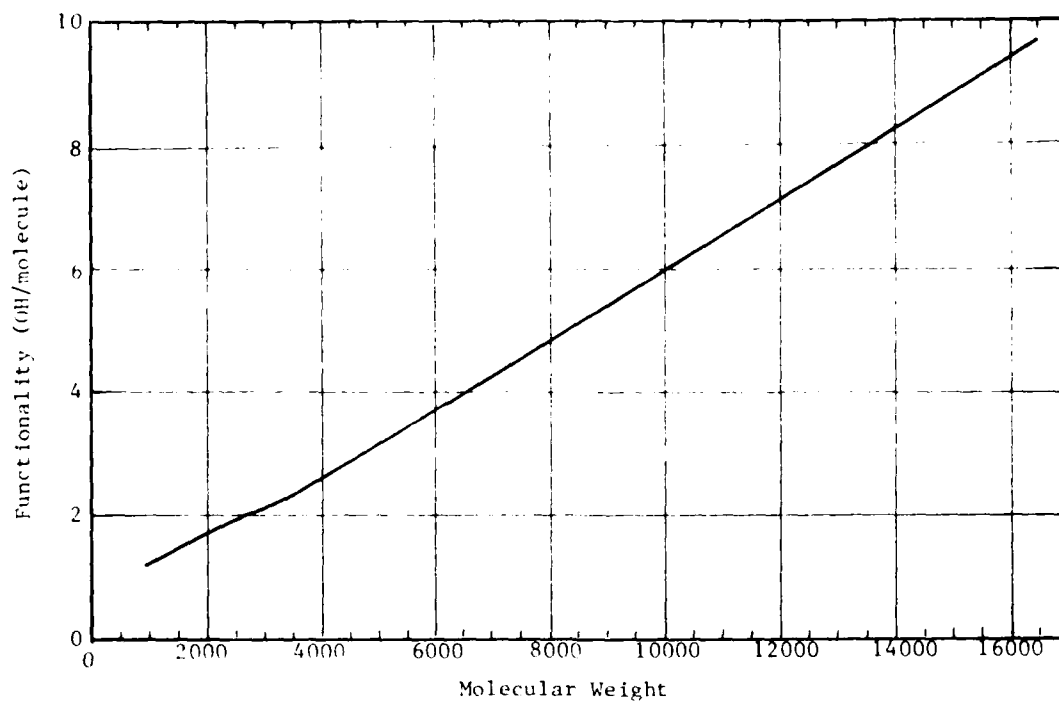


Figure 2. Functionality versus molecular weight.

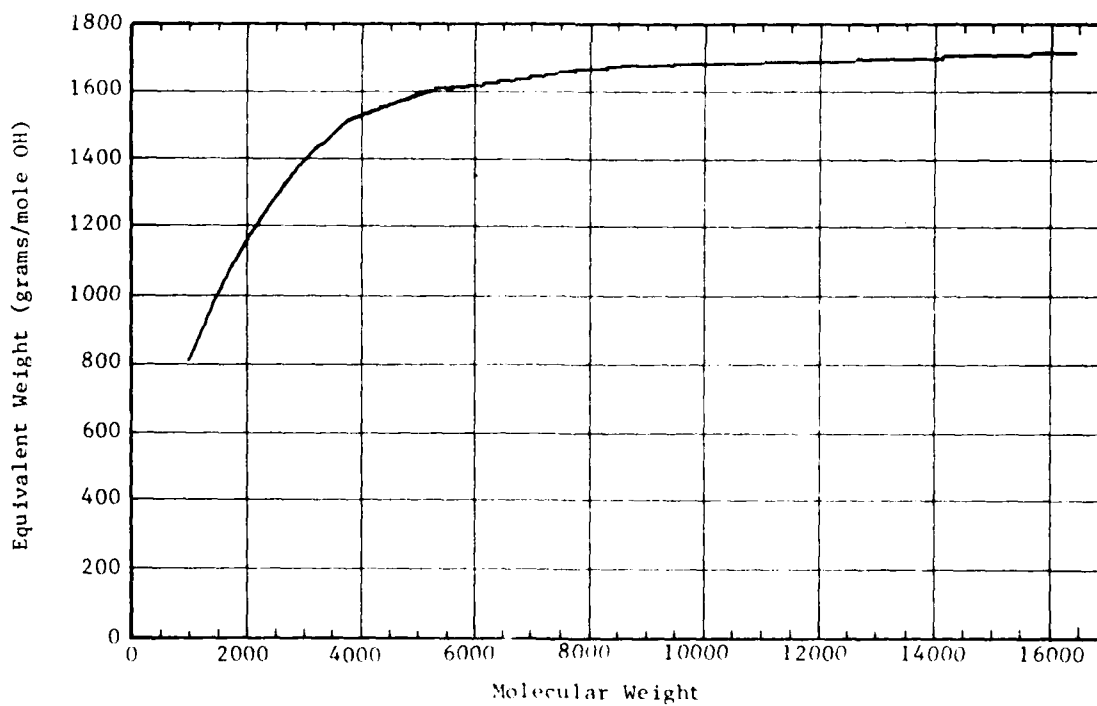


Figure 3. Equivalent weight versus molecular weight.

Table 9. Reaction-to-reaction Variation of F_n

<u>RUN</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>
14-2	13	$2.26 \pm (3.0\%)$
14-3	17	$2.18 \pm (5.6\%)$
17-1	12	$2.22 \pm (4.8\%)$
14-1	10	$2.17 \pm (4.5\%)$
14-4	17	$2.23 \pm (3.2\%)$
17-2	13	$2.18 \pm (2.8\%)$

Table 10. Day-to-day Variation of F_n

14-2			14-3		17-1	
<u>DAY</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>
1	3	$2.29 \pm (3.1\%)$	3	$2.09 \pm (.3\%)$	--	--
2	5	$2.23 \pm (1.1\%)$	5	$2.09 \pm (1.6\%)$	5	$2.29 \pm (2.6\%)$
3	2	$2.33 \pm (.6\%)$	2	$2.21 \pm (2.2\%)$	2	$2.18 \pm (5.8\%)$
14	4	$1.99 \pm (2.2\%)$	3	$1.94 \pm (3.9\%)$	2	$2.04 \pm (5.0\%)$
15	4	$2.31 \pm (6.4\%)$	9	$2.41 \pm (5.9\%)$	2	$2.28 \pm (0.9\%)$

14-1			14-4		17-2	
<u>DAY</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>	<u>NR OF ANALYSIS</u>	<u>F_n</u>
1	3	$2.21 \pm (4.7\%)$	3	$2.20 \pm (2.8\%)$	3	$2.23 \pm (2.0\%)$
2	--	--	5	$2.23 \pm (3.4\%)$	5	$2.21 \pm (1.6\%)$
3	2	$2.22 \pm (.6\%)$	--	--	--	--
14	3	$1.92 \pm (2.1\%)$	4	$2.20 \pm (6.1\%)$	3	$2.16 \pm (.8\%)$
15	2	$2.23 \pm (3.5\%)$	4	$2.20 \pm (2.4\%)$	--	--

The procedure has been evaluated and found to have an accuracy for \bar{M}_N of better than 4 percent and a precision of better than 3 percent. The accuracy and precision of F_n determined by this procedure are generally better than 5 percent and 4 percent, respectively. Comparison of this procedure with the currently accepted procedure cuts the analysis time from several days to a few hours and is at least twice as accurate.

These improvements will remove most of the objections to routine determination of the molecular weight and functionality of polymers. During the last year of this project several propellant manufacturing companies have shown interest in the procedure and asked for details. At least two are examining this procedure or their own modification of it for in-house use.

It is hoped that, as more data on the molecular weight distribution and functionality distribution of polymers are amassed, a better correlation of these data to the properties of propellants can be derived. At the moment, the most useful information this procedure will develop is the average molecular weight and functionality of the polymer.

APPENDIX A
DATA REDUCTION

The area versus time data were obtained from the refractive index and ultraviolet detectors by two A/D converters and transmitted to a Hewlett-Packard 21 MX computer and stored in memory files. Following completion of the GPC run, the attached basic language program was activated. Several options are available with this program. If an automatic liquid sampler, which can transmit the sample bottle number to the computer, is not available, then, by turning on Switch 15 on the computer front, sample parameters can be entered following each run.

By turning on Switch 14 it is possible to monitor the computer's decision process as it searches the data for the sample and determines the start and stop times of the peak. If the window selected by the computer is not acceptable, it can be modified. The values used in the calibration can be printed along with the report. If a functionality report is not desired, it can be suppressed by giving a negative response.

To use this program, the following procedure must be followed:

- Calibrate your system for molecular weight using the universal calibration procedure.
- Determine the slope(s) of the calibration line of (Log M) [N] versus elution volume.
 - Enter the slope(s) in lines 170-190 and the intercept(s) in lines 200-220.
 - Calibrate the flow rate by determining the seconds for 25 ml to elute.
 - Enter the time in line 150.
 - If there is more than one slope to the calibration, enter the break points in lines 120-130.
- Determine the response factor of the polymer in the RI and enter in lines 6060 and 6065.
- Determine the response factor for the derivative in the UV and enter the values in lines 6090 and 6095. In this system, channel 0 was the UV signal and channel 1 was the RI. If set up differently, the new values should be entered in lines 230, 240, 6020, 6025, and 6565.

A Waters Associates Wisp 710 was used in this project. It was monitored by the computer through the connection described in Appendix B. If this system is used, then by turning on Switch 13, the computer will request the bottle number, name, and intrinsic viscosity of each sample from the Wisp 710. Without such a system, the sample identification and intrinsic viscosity may be entered by the user by turning on Switch 15.

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8: BINDER      8 MAR, 1981 10:08
10 COM T(3),H(48),A(240),E(240),F(240),G(240),C(13)
20 DIM D$(48),T$(14),U$(13),P(210),O(210),N(10),S(20),I(16)
30 IF T(1)<5 OR T(1)>30 THEN LET T(1)=9.5
40 IF T(2)<5 OR T(2)>30 THEN LET T(2)=17.5
50 LET T$=" HOURS DATE "
60 LET U$=" % OF POLYMER"
70 LET D$="JAN FEB MAR APR MAY JUNE JULY AUG SEPT OCT NOV DEC "
80 LET A=D1=D2=E1=E2=E3=E4=F1=F2=F3=F4=F5=F6=F7=G=H=0
90 LET K1=K2=K3=K4=N1=N2=S1=S2=S3=S4=N1=N2=D1=0
100 LET N$="0123456789"
110 LET B$=" : "
118 REM
119 REM *** CALIBRATION BREAK POINTS ***
120 LET V1=23.41
130 LET V2=27.185
131 REM
140 REM ***F IS SECONDS FOR 25 ML TO ELUTE***
150 LET F=758
151 REM
160 LET F=1500/F
165 IF SWR(13)=1 THEN GOSUB 3500
167 REM
168 REM *** CALIBRATION SLOPE ***
170 LET B(1)=-.692498
180 LET B(2)=-.314627
190 LET B(3)=-.158089
197 REM
198 REM *** CALIBRATION INTERCEPT ***
200 LET C(1)=20.3336
210 LET C(2)=11.4876
220 LET C(3)=7.23215
227 REM
228 REM *** INITIALIZES CONTACT WITH CHANNEL 1 ***
230 INIT (M$,1,E)
240 LET B5=1
241 REM
250 PEAK (1,H$,T,W,C1,E)
260 LET W=60/ABS(W)
270 GOSUB 4000
280 IF SWR(15)=0 THEN 330
285 PRINT "SAMPLE ID";
290 INPUT S$
295 PRINT "INTRINSIC VISCOSITY";
300 INPUT V(1)
305 PRINT "DO YOU WANT A FUNCTIONALITY REPORT (Y/N)";
310 INPUT C$
311 IF C$(1,1)="Y" THEN 315
312 IF C$(1,1)="N" THEN 315
313 GOTO 305
315 PRINT "THERE ARE ";W;" SLICES PER MINUTE."
320 PRINT "SELECT THE INTERVAL BETWEEN THE SLICES YOU WANT PRINTED."
325 INPUT T(3)
330 LET B=INT((W*T(1))+.5)
335 GOSUB 1000
340 GOSUB 1500
345 IF SWR(15)=0 THEN 450
350 PRINT "PEAKS START AT ";T2;" AND END AT ";T3
355 PRINT "M W D CALCULATION LIMITS ARE NOW ";T(1);" TO ";T(2)
360 PRINT "DO YOU WANT TO CHANGE THE M W D CALCULATION LIMITS (Y/N)";
365 INPUT X$
370 IF X$(1,1)="Y" THEN 385
375 IF X$(1,1)!="N" THEN 350
380 GOTO 450
385 PRINT "DO YOU WANT TO CHANGE THE START, END, OR BOTH";

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390 INPUT X$
395 IF X$(1,1)="S" THEN 420
400 IF X$(1,1)="E" THEN 435
405 IF X$(1,1)="B" THEN 420
410 PRINT "RESPONSE MUST BE START , END , OR BOTH !"
415 GOTO 385
420 PRINT "INITIAL TIME IN MINUTES";
425 INPUT T(1)
430 IF X$(1,1)="S" THEN 445
435 PRINT "FINAL TIME IN MINUTES";
440 INPUT T(2)
445 GOTO 330
450 GOSUB 2000
455 IF SWR(15)=1 THEN GOSUB 3100
460 GOSUB 3000
465 IF C$(1,1)="Y" THEN GOSUB 6000
470 GOSUB 3000
475 STOP
1000 REM *** CALCULATES NOISE AND BASELINE CONSTANTS ***
1001 FOR J=1 TO 5
1002 LET A(J)=0
1003 NEXT J
1004 LET S1=S2=R=0
1005 LET N=25
1010 FOR I=B-24 TO B
1015 PEAK (I,N$,T,A,C1,E)
1020 LET S1=S1+A
1025 NEXT I
1030 LET M=S1/N
1035 FOR I=B-24 TO B
1040 PEAK (I,N$,T,A,C1,E)
1045 LET S2=S2+(A-M)^2
1050 NEXT I
1055 IF S2 <= 0 THEN LET S2=.1
1060 LET D1=SQR(S2/(N-1))
1070 IF D1<1.50000E-02 THEN LET D1=1.50000E-02
1075 LET D2=D1*5
1080 LET R2=INT((W*60/F)+.5)
1085 FOR I=R2-9 TO R2
1090 PEAK (I,N$,T,A,C1,E)
1095 LET R=R+A
1100 NEXT I
1105 LET R=R/10
1110 LET B1=(R-M)/((R2-5)-B)
1115 LET B2=M-B1*B
1120 RETURN
1500 REM *** DETERMINES START OF FIRST PEAK ABOVE .5 STANDARD DEVIATIONS ***
1505 IF SWR(14)=1 THEN PRINT "LOOKING FOR START OF PEAK OVER ";D2
1510 PRINT
1515 IF SWR(14)=1 THEN PRINT "D1 = ";D1
1520 PRINT
1525 LET P1=B-2
1535 PEAK (P1,N$,T,A1,C1,E)
1540 LET A1=A1-(B1*P1+B2)
1550 LET T2=T
1555 LET C=1
1560 FOR I=B-1 TO R2
1565 GOTO 1590
1570 IF SWR(14)=1 THEN PRINT "I =";I;" T =";T;TAB(25);"AREA =";A2;
1571 IF SWR(14)=1 THEN PRINT TAB(45);" F1 =";F1
1575 NEXT I
1580 PRINT "NO PEAKS IN THE RI !!!"
1585 STOP
1590 PEAK (I,N$,T,A2,C1,E)
1591 LET A2=A2-(B1*I+B2)
1595 IF A2>D2 THEN GOTO C OF 1655,1745

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1600 LET A(5)=F1=0
1605 IF (A2-A1) >= D1 THEN LET A(5)=1
1610 FOR J=1 TO 4
1615 LET A(J)=A(J+1)
1620 LET F1=F1+A(J)
1625 NEXT J
1630 IF F1 >= 3 AND C=1 THEN LET T2=T-.2
1635 IF F1 >= 3 AND C=2 THEN LET T3=T-.2
1640 IF F1 >= 3 THEN GOTO C OF 1655,1745
1645 LET A1=A2
1650 GOTO C OF 1570,1735
1655 REM *** DETERMINES END OF LAST PEAK ABOVE +5 STANDARD DEVIATIONS
1660 PRINT
1665 IF SWR(14)=1 THEN PRINT "LOOPING FOR END OF LAST PEAK OVER ";D2
1670 PRINT
1675 LET J3=I-3
1680 PEAK (J3,N$,T2,A,C1,E)
1685 LET R2=INT(T(2)+W+.5)+5
1695 PEAK (R2,N$,T,A1,C1,E)
1710 LET T3=T
1715 LET F1=0
1720 LET C=2
1725 FOR I=R2-1 TO J3+3 STEP -1
1730 GOTO 1590
1735 IF SWR(14)=1 THEN PRINT "I =";I;" T =";T;TAB(25);" AREA =";A2;
1736 IF SWR(14)=1 THEN PRINT TAB(45);" F1 =";F1
1740 NEXT I
1745 LET J4=I+3
1750 PEAK (J4,N$,T3,A,C1,E)
1755 RETURN
2000 REM *** GPC REPORT ***
2005 PRINT
2010 PRINT TAB(15);"GEL PERMIATION CHROMATOGRAPHIC REPORT"
2015 PRINT
2020 PRINT TAB(15);"TIME ";B$;T$;D(1);D$(D(2),D(2)+30);" ";D(3)
2025 PRINT
2030 PRINT "SAMPLE : ";S$;TAB(40);"INTRINSIC VISCOSITY :";V(1)
2035 PRINT
2040 PRINT " FLOW"," AVE.B-L"," SLOPE"," INTERCEPT"," STD.DEV."
2045 PRINT F,M,B1,B2,D1
2050 PRINT " ML/MIN"," AREA CTS."," AREA CTS./SL"," AREA CTS."
2055 PRINT
2060 PRINT "M W D COMPUTED BETWEEN ";T2;"MIN. AND ";T3;"MIN."
2065 PRINT
2070 PRINT "V1 =";V1;"ML. V2 =";V2;"ML."
2075 PRINT
2080 PRINT "EL. TIME","EL. VOL.," "MOL. WT.," "CORR. AREA","CUM. %"
2085 PRINT
2090 FOR I=J3 TO J4
2095 GOSUB 2500
2100 LET A9=A9+A
2105 NEXT I
2110 FOR I=J3 TO J4
2115 GOSUB 2500
2120 GOSUB 5500
2125 LET G=G+A*100/A9
2130 LET N1=N1+A*M1
2135 LET W1=W1+A*M1
2140 LET Z1=Z1+A*N1+2
2145 LET H=H+1
2150 IF H=1 THEN PRINT T,T+F,M1,A,G
2155 IF H=T(3) THEN LET H=0
2160 NEXT I
2165 PRINT
2170 LET M9=SQR((A9/N1+.2)+(W1/A9+.2+.2)
2175 PRINT " TOTAL AREA"," MH"," MH"," MC"," MO"

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2180 PRINT A9,A9 N1,W1 A9,Z1+W1,M9
2185 LET W2=A9 N1
2190 PRINT
2195 PRINT " ", "POLYDISPERSITY", " ", "SKEWNESS", " ", "ASYMMETRY"
2200 LET S=(Z1 N1)-(Z+A9 N1 Z1+W1)+(Z+A9 N1)-(Z1)
2205 PRINT " ", W1+N1 A9 Z,S (A9 N1)-(Z,S (W1 N1)-(A9 N1)-(Z1 1.5)
2210 PRINT
2215 PRINT
2220 GOSUB 2700
2225 PRINT
2230 PRINT "POLYMER PEAK MAXIMUM"
2240 GOSUB 5500
2245 PRINT T1;" MIN. ";P;" ML. MOL. WT. OF THE PEAK IS ";M1
2250 RETURN
2500 REM *** GET A SLICE AND SUBTRACT THE BASELINE ***
2505 PEAK (I,N$,T,A1,C1,E)
2510 LET A=A1-(B1+I+B2)
2515 IF A=0 THEN LET A=0
2520 RETURN
2700 REM *** FIND PEAK MAXIMUM ***
2705 LET P=A2=0
2710 FOR I=J3 TO J4
2715 PEAK (I,N$,T,A1,C1,E)
2720 LET A=A1-(B1+I+B2)
2725 IF A >= A2 THEN LET P=T+P
2730 IF A >= A2 THEN LET T1=T
2735 IF A >= A2 THEN LET A2=A
2740 NEXT I
2741 LET T=T1
2745 RETURN
3000 REM *** SKIP 4 LINES ***
3005 FOR I=1 TO 4
3010 PRINT
3015 NEXT I
3020 RETURN
3100 REM *** CALIBRATION CONSTANTS ***
3105 GOSUB 3000
3110 PRINT "*** CALIBRATION VALUES ***"
3115 PRINT
3120 FOR I=1 TO 3
3125 PRINT "SLOPE ";I;" =";B(I),"INTERCEPT ";I;" =";C(I)
3130 NEXT I
3135 RETURN
3500 REM *** SET UP AUTOMATIC SAMPLING LIST ***
3525 INDVC "T1",E
3530 PRINT "*****AUTOMATIC SAMPLING LIST*****"
3535 PRINT "IS THIS A NEW LIST";
3540 INPUT N$
3545 IF X$(1,1)="#Y" THEN 3665
3550 FOR I=1 TO 48
3555 LET N(I)=0
3560 NEXT I
3565 PRINT "AFTER THE LAST SAMPLE ENTER BOTTLE NUMBER 0"
3570 PRINT
3575 PRINT "BOTTLE #","SAMPLE NAME","VISCOSITY"
3580 PRINT
3585 FOR I=1 TO 48
3590 INPUT B,S$,V
3595 IF B=0 THEN 3665
3600 IF B <= 12 THEN 3650
3605 IF B <= 24 THEN 3630
3610 IF B <= 36 THEN 3640
3615 IF B > 48 THEN 3795
3620 LET G=(B-36)*20-19,(B-36)+20)=S$
3625 GOTO 3655
3630 LET E=(B-12)*20-19,(B-12)+20)=S$

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3635 GOTO 3655
3640 LET F#(B-24+20-19,B-24+20)=S#
3645 GOTO 3655
3650 LET A#(B+20-19,B+20)=S#
3655 LET NCB1=V
3660 NEXT I
3665 PRINT "WANT A LISTING (Y/N)";
3670 INPUT X#
3674 IF X#(1,1)="Y" THEN 3680
3675 IF X#(1,1)="N" THEN 3760
3676 GOTO 3665
3680 PRINT TAB(5); "BOTTLE #"; TAB(20); "SAMPLE NAME"; TAB(55); "VISCOSITY"
3685 PRINT
3690 FOR I=1 TO 48
3695 IF NCB1 0 THEN 3705
3700 GOTO 3755
3705 IF I = 12 THEN 3750
3710 IF I = 24 THEN 3740
3715 IF I = 36 THEN 3730
3720 PRINT TAB(5); I; TAB(20); G#(I-36+20-19,I-36+20); TAB(55); NCB1
3725 GOTO 3755
3730 PRINT TAB(5); I; TAB(20); F#(I-24+20-19,I-24+20); TAB(55); NCB1
3735 GOTO 3755
3740 PRINT TAB(5); I; TAB(20); E#(I-12+20-19,I-12+20); TAB(55); NCB1
3745 GOTO 3755
3750 PRINT TAB(5); I; TAB(20); A#(I+20-19,I+20); TAB(55); NCB1
3755 NEXT I
3760 PRINT "ANY CHANGES (Y/N)";
3765 INPUT X#
3769 IF X#(1,1)="Y" THEN 3570
3770 IF X#(1,1)="N" THEN 3780
3775 GOTO 3760
3780 PRINT
3785 PRINT "PREPARATION OF AUTO RUN COMPLETE"
3790 GOTO 9999
3795 PRINT "BOTTLE NUMBER "; B; " DOES NOT EXIST!!!"
3800 PRINT "ONLY BOTTLES 1 TO 48 ARE ACCEPTED."
3805 PRINT "IF YOU ARE FINISHED ENTER 0 FOR THE BOTTLE NUMBER."
3810 PRINT "NOW TRY AGAIN."
3815 GOTO 3570
4000 REM*** CHECK ECM STATUS, POWER FAILURE, OR NORMAL END OF RUN***
4005 GOSUB 5000
4010 PRINT
4015 BIN 2,I#,E
4020 IF E=0 THEN 4035
4025 PRINT "ECM DOWN - ERROR CODE = "; E
4030 GOTO 4375
4035 IF I$(7,7)="1" THEN 4050
4040 PRINT "POWER FAILURE DETECTED AT WISP HPLC"
4045 GOTO 4375
4050 IF I$(4,4)="1" THEN 4065
4055 PRINT "END OF RUN INDICATED BY WISP"
4060 GOTO 4150
4065 REM*** START 2 MINUTE CLOCK***
4070 LET T1=TIM(-1)
4075 LET F1=0
4080 LET A=TIM(-1)
4085 IF A=T1 THEN 4080
4090 LET F1=F1+1
4095 LET T1=A
4100 REM*** CHECK PAUSE AND STOP***
4105 BIN 2,I#,E
4110 IF E#0 THEN 4025
4115 IF I$(3,3)="1" THEN 4170
4120 IF I$(4,4)="0" THEN 4055
4125 REM *** ADD WHEN USING SCM *** IF F1=120 THEN 4080 ***

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4130 REM***SAMPLE READY, RETURN TO ALS***
4135 GOSUB 4400
4140 REM *** 4145 TO 4155 TO BE ADDED WHEN USING BOM ***
4145 REM *** PRINT " BOTTLE # ";B;" READY FOR INJECTION"
4150 REM *** GOSUB 5000
4155 REM *** PRINT " RETURN CONTROL TO ALS ";B#
4160 GOSUB 4400
4165 GOTO 4450
4170 GOSUB 4440
4175 PRINT "PAUSE IN SAMPLING INDICATED BY WISE"
4180 RETURN
4185 REM***START 15 MIN CLOCK***
4190 LET F1=F2=0
4195 LET T1=TIM(0)
4200 REM***CHECK PURGE***
4205 IF I$(6,6)="1" THEN 4220
4210 IF F2=1 THEN 4245
4215 GOTO 4260
4220 IF F2=1 THEN 4260
4225 LET F2=1
4230 GOSUB 5000
4235 PRINT TAB(5);"PURGE INITIATED ";B#
4240 GOTO 4260
4245 LET F2=0
4250 GOSUB 5000
4255 PRINT TAB(5);"PURGE COMPLETED ";B#
4260 REM*** CHECK SKIP***
4265 IF I$(5,5)="1" THEN 4275
4270 GOTO 4295
4275 GOSUB 4400
4280 GOSUB 5000
4285 PRINT TAB(5);"BOTTLE # ";B;" CANNOT BE INJECTED ";B#
4290 GOTO 4350
4295 REM*** START SAMPLING DRILL AGAIN***
4300 IF I$(3,3)="1" THEN 4130
4305 GOTO 4065
4310 LET A=TIM(0)
4315 IF A=T1 THEN 4335
4320 LET F1=F1+1
4325 LET T1=A
4330 IF F1>15 THEN 4350
4335 BIN 2,I#,E
4340 IF E#0 THEN 4025
4345 GOTO 4200
4350 PRINT "UNRECOVERABLE ERROR CONDITION PERCEIVED"
4355 REM***SHUT OFF HPLC***
4360 OFF 2,3,E
4365 IF E#0 THEN 4025
4370 REM*** PAUSE SEQUENCE***
4375 AUTO -1,1
4380 PRINT "RUN TERMINATED, SEQUENCE HALTED"
4385 GOTO 9999
4400 REM*****SUBROUTINE BOTTLE*****
4405 REM*****COMPUTE BOTTLE NUMBER FROM BIN INPUT*****
4410 REM*****
4415 LET B=0
4420 FOR I=1 TO 4
4425 IF I$(I+8,I+8)="1" THEN LET B=B+2*(I-1)
4430 NEXT I
4435 IF I$(13,13)="1" THEN LET B=B+10
4440 IF I$(14,14)="1" THEN LET B=B+20
4445 RETURN
4450 REM*** SELECT SAMPLE NAME AND VISCOSITY ***
4455 IF B=1 THEN 9999
4460 IF B=12 THEN 4510
4465 IF B=24 THEN 4500

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4470 IF B = 36 THEN 4490
4475 IF B = 48 THEN 9999
4480 LET S$=G$(B-36)+20-19, (B-36)+20)
4485 GOTO 4515
4490 LET S$=F$(B-24)+20-19, (B-24)+20)
4495 GOTO 4515
4500 LET S$=E$(B-12)+20-19, (B-12)+20)
4505 GOTO 4515
4510 LET S$=A$(B+20-19, B+20)
4515 LET V(1)=N(B)
4520 LET V(3)=B
4525 RETURN
5000 REM *** GET THE DATE AND TIME ***
5005 LET I=0
5010 FOR J=1 TO 0 STEP -1
5015 LET N=TIM-J
5020 IF N#0 THEN 5035
5025 LET B$(I+1,1+2)=""00"
5030 GOTO 5060
5035 FOR K=2 TO 1 STEP -1
5040 LET L=INT(.10*(N-INT(N*.10))*.5)
5045 LET N=INT(N*.10)
5050 LET B$(I+1,1+K)=N$(L+1,L+1)
5055 NEXT K
5060 LET I=3
5065 NEXT J
5070 FOR I=2 TO 4
5075 LET D(I-1)=TIM-I
5080 NEXT I
5085 LET D(2)=D(2)+4-3
5090 RETURN
5500 REM *** CALCULATES MOL. WT. FOR TIME T ***
5505 LET K=1
5510 IF T+F >= V1 THEN LET K=2
5515 IF T+F >= V2 THEN LET K=3
5520 LET M1=.10*(B(K)+T+F)+C(K)+V(1)
5525 RETURN
6000 REM *** SUBTRACTS BASELINE AND STORES IF CORRECTED APERS ***
6005 LET A9=0
6010 GOSUB 6045
6011 REM
6012 REM *** INITIALIZES CONTACT WITH CHANNEL 0 ***
6020 INIT (M$,0,E)
6025 LET B5=0
6026 REM
6030 GOSUB 1000
6035 GOSUB 6045
6040 GOTO 6120
6045 FOR I=J3+1-B5 TO J4+1-B5
6050 PEAK (I,N$,T,A1,C1,E)
6055 IF B5=0 THEN 6090
6057 REM
6058 REM *** RESPONSE FACTOR FOR P1 ***
6060 LET R5=1.80661E-02
6065 LET R6=.420142
6066 REM
6070 LET R(I-J3+1)=(A1-(B1*I+B2)-R5)*R6
6075 IF R(I-J3+1) <= 0 THEN LET R(I-J3+1)=1.00000E-10
6080 LET A9=A9+R(I-J3+1)
6085 GOTO 6110
6087 REM
6088 REM *** RESPONSE FACTOR FOR UV ***
6090 LET U5=8.63600E-05
6095 LET U6=1513
6096 REM
6100 LET U(I-J3)=(A1-(B1*I+B2)-U6)+U5

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6105 IF U(1-J3) = 0 THEN LET U(1-J3)=1.00000E-10
6110 NEXT I
6115 RETURN
6120 IF SWR(14)=0 THEN 6500
6125 PRINT "SLICE";TAB(25);"PI";TAB(45);"UV"
6130 FOR I=1 TO J4-J3+1 STEP 1(3)
6135 PRINT I+J3-1;TAB(25);P(I);TAB(45);U(I)
6140 NEXT I
6145 GOTO 6500
6500 REM *** FUNCTIONALITY REPORT ***
6501 PRINT "TOTAL AMT. POLYMER INJECTED = ";A9 1.00000E+06;"MG"
6505 PRINT
6510 GOSUB 3000
6515 PRINT TAB(25);"FUNCTIONALITY REPORT"
6520 PRINT
6525 PRINT TAB(15);"TIME ";B$;T$;D(1);D$(D(2),D(2)+30);" ";D(3)
6530 PRINT
6535 PRINT "SAMPLE ";S$
6540 PRINT
6545 PRINT "AVG. FUNC.";TAB(12);"AVG. EO. WT.";TAB(27);
6550 PRINT "MN";TAB(38);"FOR MOL. WT. RANGE";TAB(66);U$
6555 PRINT "COH MOL.";TAB(12);"G MOLE"
6560 PRINT
6563 REM
6564 REM *** INITIALIZES CONTACT WITH CHANNEL 1 ***
6565 INIT (M$,1,E)
6566 REM
6570 LET H=F1=F2=F3=F4=F5=F6=F7=F8=0
6575 FOR J=1 TO J4-J3+1
6580 LET I=J+J3-1
6585 PEAR (I,N$,T,A,C1,E)
6590 GOSUB 5500
6595 LET F2=F2+U(I)
6600 LET F5=F5+(R(I)-M1)
6605 LET F6=F6+U(I)
6625 LET F1=F1+(R(I)-M1)
6630 LET F4=F4+R(I)
6635 LET F7=F7+M1+U(I)
6645 IF H=0 THEN LET M2=M1
6650 LET M3=M1
6655 IF J=J4-J3+1 THEN 6670
6660 IF H=0 THEN LET H=1
6670 IF (F4/A9)*100/10 THEN 6695
6673 LET F8=F4/F1
6675 LET F1=F6/F1
6680 PRINT F1;TAB(12);F4 F6;TAB(24);F8;TAB(36);M2;TAB(48);"TO ";
6685 PRINT M3;TAB(68);(F4/A9)*100
6690 LET H=F1=F4=F8=0
6695 NEXT J
6700 PRINT
6705 PRINT "FN = ";M2+F2 A9,"FW = "F7 A9
6710 PRINT "AVG. FUNCTIONALITY OF POLYMER = ";F2 F5;" OH MOLECULE"
6715 PRINT "AVG. EO. WT. OF POLYMER =";A9 F2;"G POLYMER MOLE OH"
6720 RETURN
9999 END

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APPENDIX B
WISP BCD BOARD OPERATION DESCRIPTION

The interface board connects to the WISP data and address buses. Sample bottle number and status information are passed to the interface when the CPU addresses the board. The address is decoded by logic elements on the board routing the data to two registers that connect to the output lines. Information can be stored in the registers in either a positive logic or a negative logic sense, depending on the setting of the selector switch on the board. Also on the board is a bus driver that enables the WISP standby input signal to be transmitted to the CPU over the data bus. The signal is placed on the bus only when the CPU addresses the driver. The schematic for the WISP 710B BCD Board and the wiring adapter to connect the WISP to the ECM are presented in Figures 4 and 5, respectively.

- Start and Stop Signals. The start and stop signals are pulses of one second duration. The start pulse occurs at the moment of injection. The stop pulse occurs at the end of the programmed run time. If an equilibration delay time is programmed, it will follow the stop pulse.

- Sample Bottle Number. The number presented by the interface is the number of the sample bottle that is positioned under the injector. This number is continuously updated and matches the number on the front panel display. The BCD format of this number is decoded by summing the values of the lines that are at logic 1. For example, if negative logic is used, this output,

1 low	10 high
2 high	20 low
4 high	40 high
8 low	80 high

represents sample number 29.

- Pause. Logic 1 indicates a temporary interruption in the injection sequence. This may be due to a volume verification failure or a temporary loss of air pressure. The output returns to logic 0 when the WISP resumes injections.

- Run. Logic 1 indicates that RUN mode is entered. Logic 0 indicates termination of the injection sequence (STOP mode). A change to STOP mode may be either the normal completion of the programmed injections or a nontemporary error condition such as a mechanical failure.

- Skip Injection. A logic 1 is output if the WISP skips a programmed injection. This occurs if the sample fails to pass the volume verification test two consecutive times. The signal is of several seconds duration. Simultaneously, the BCD output presents the sample bottle number of the skipped injection.

- Purge. A logic 1 indicates that the WISP is performing a purge. This may be the standard purge or the flowing purge used when the sample volume is greater than 150 μ l. The output has the same duration as the purging process.

- Power On. The output is high (>2.4V) whenever the WISP has power and is ON. This permits a data system on a separate power line to monitor the WISP line for power failures.

- WISP Standby. The input line is tested by the CPU when the WISP has drawn a sample and is ready to perform the injection. If the input is high ($>2.4V$), the injection is made immediately. If the input is low ($0.4V$) (or grounded), the WISP does not make the injection until the input changes to the high state. Note that it is only immediately prior to injection that the state-of-the-input line is examined. This line may assume any state at other times without affecting the operation of the WISP. A disconnected input is interpreted as being high.

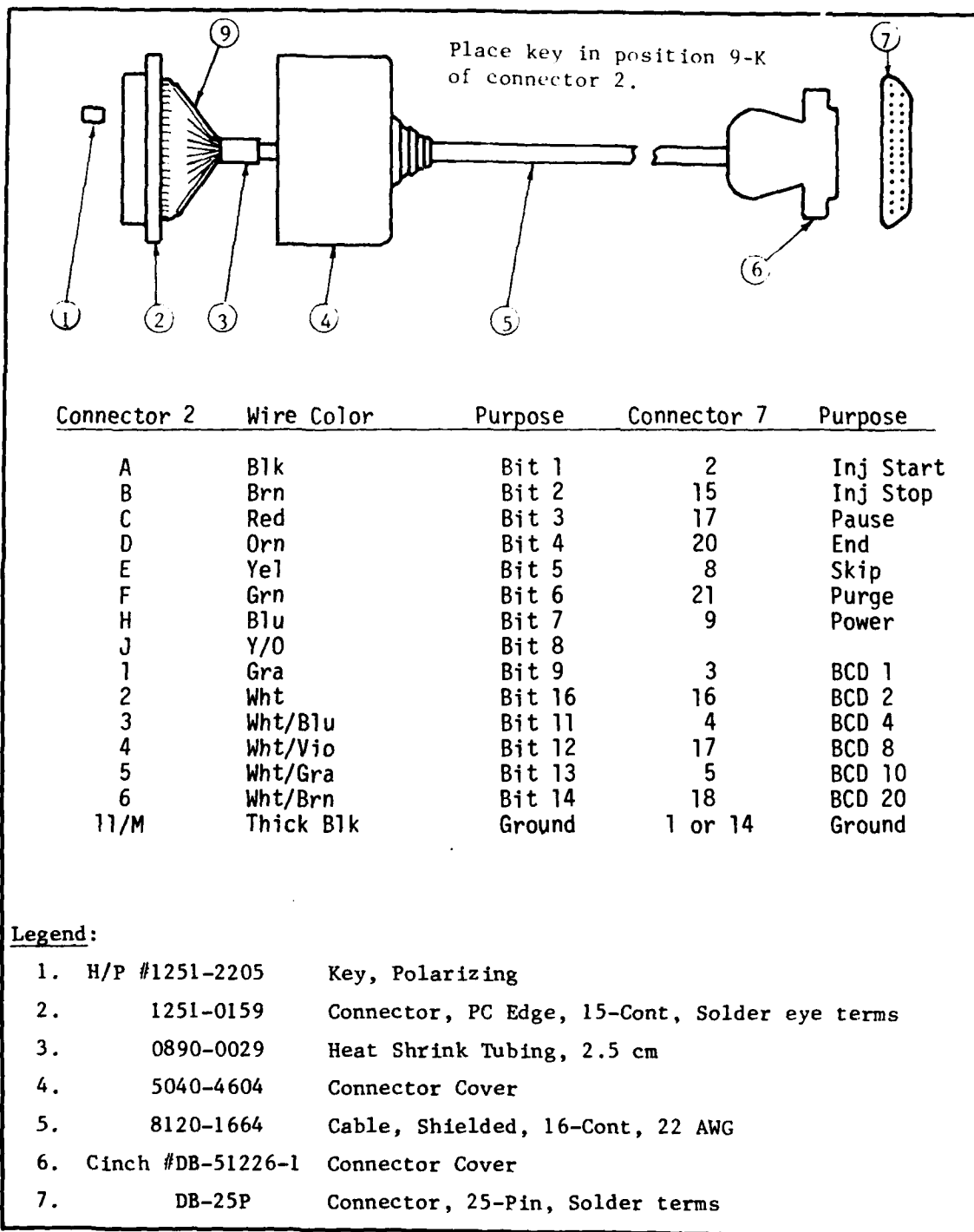


Figure 5. WISP/ECM binary input cable.

APPENDIX C
DERIVATIZATION PROCEDURE

For a homogenous hydroxy-terminated polymer of about 2000 \bar{M}_n , place about 2.5 g in a 25-ml volumetric flask and fill to the mark with LC grade tetrahydrofuran. Mix the sample well to obtain a homogenous solution. Into a small cone-bottom vial or bottle (5 ml was used in this work) weigh at least 0.18 g of 3,5 dinitrobenzoylchloride (DNBC) (0.8 millimoles), pipette in 4 ml of the polymer solution (0.4 millimoles of hydroxyl groups). The 3,5 DNBC will dissolve in the THF in a short time depending on the crystal size. After the 3,5 DNBC has dissolved, add 2 to 3 drops of N-methylimidazol. A white precipitate will form instantly. Shake the sealed vial well for a minute and warm to 60°C for 15 minutes to complete the reaction. Evaporate the THF under a stream of nitrogen with gentle heating. Dissolve the residue in 3 ml of diethylether and wash twice with one ml of 5 percent NaHCO_3 and twice with one ml of water. Occasionally an emulsion may develop; but addition of more ether usually resolves the problem. The ether layer is then pipetted into a syringe fitted with a Waters Associates sample filtration kit. The sample is filtered into a vial and is then ready for chromatographic analysis.

REFERENCES

1. "Characterization of R45-M," Final Report, AFRPL-TR-74-64, Nov. 1974.
2. "Statistical Correlation of HB Polymer Properties with the Mechanical Properties of TP-H1011 Propellant," presented to the 8th Annual JANNAF Propellant Characterization Subcommittee, Boulder, Colorado, June 1977.
3. "Improved HTPB Prepolymers for Tactical Propellants," Final Report, AFRPL-TR-73-64, August 1973.
4. "Binder Properties Optimization," Final Report, AFRPL-TR-77-93, ADB025835, Nov. 1977.
5. "Improved Specifications for Composite Propellant Binders for Army Weapon Systems," USAMICOM Technical Report T-79-76, July 1979.
6. Anderson, J., S. Baczek, H. Adams, and L. Vescelius, J. Appl. Polym. Sci., 19, 2255 (1975).
7. Baczek, S., J. Anderson, and H. Adams, J. Appl. Polym. Sci., 19, 2269 (1975).
8. "Vapor Pressure Osmometer; An Interlaboratory Evaluation," Propellant Characterization Working Group, Chemical Propulsion Information Agency, August 1976.
9. Adams, H., et al., J. Appl. Polym. Sci., 17, 269 (1973).
10. Mori, S., J. Appl. Polym. Sci., 21, 1921 (1977).
11. Mori, S., J. Chromatogr., 174, 23 (1979).
12. Baker, D., and S. George, Amer. Lab 12 (1), 41 (1980).
13. Landuyt, D. Van, and C. Huskins, Poly. Let., 6, 643 (1968).
14. Grubisic, Z., et al., Poly Let., 5, 753 (1967).
15. Cazes, J. and R. Dobbins, Poly Let., 8, 785 (1970).
16. Grubisic, Z., M. Picot, P. Gramain, and H. Benoit, J. Appl. Polym. Sci., 16, 2931 (1972).
17. McCrackin, F., J. Appl. Polym. Sci., 21, 191 (1977).
18. Kato, Y., et al., J. Appl. Polym. Sci., 21, 577 (1977).
19. Mahabadi, H., and K. O'Driscoll, J. Appl. Polym. Sci., 21, 1283 (1977).
20. Carignan, Y., and E. Turngren, "Development of a Method of Gel Permeation Chromatography (GPC) for Analyzing Cellulose Nitrates," Technical Report ARLCD-TR-77048, Nov. 1977.

REFERENCES (Concluded)

21. Dark, W., *Chromatog Sci*, 16, 274 (1978).
22. Chaplin, R., J. Haken, and J. Paddon, *J. Chromatog*, 171, 55 (1979).
23. Mori, S., *J. Chromatog*, 192, 295 (1980).
24. Scott, P., and C. Reese, *J. Chrom*, 138, 283 (1977).
25. Runyon, J., D. Barnes, J. Rudd, and L. Tung, *J. Appl. Polym. Sci.*, 13, 2359 (1969).
26. Fritz, D., A. Sahil, H. Keller, and E. Kovats, *Anal. Chem.*, 51, 7 (1979).
27. Yamashita, S., K. Sando, and S. Kohjiya, *J. Appl. Polym. Sci.*, 23, 1951 (1979).
28. Jupille, T., *American Laboratory*, 8, 85 (1976).
29. Nozawa, A., and T. Ohnuma, *J. Chromatogr*, 187, 261 (1980).
30. Bjorkvist, B., and H. Toivonen, *J. Chromatogr.*, 153, 265 (1978).
31. Ross, M., *J. Chromatogr*, 141, 107 (1977).
32. Siggia, S., "Instrumental Methods of Organic Functional Group Analysis," Wiley-Interscience, New York, pp. 1-74 (1972).
33. Blau, K. and G. King, "Handbook of Derivatives for Chromatography," Heyden, London, pp. 118-119, (1978).
34. "A User's Guide to Chromatography," Regis Chemical Co., pp. 186-187, (1976).
35. Conners, K. A., and N. K. Pandit, *Anal. Chem.*, 50 1542 (1978).
36. Carey, M. A., and H. E. Perisinger, *J. Chrom. Sci.* 10, 537 (1972).

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